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16. Abstract

The kinetics of the establishment of the oxidation-reduction potential of a titanium electrode upon contact with hydrazine was studied in different media: H_2SO_4, NaOH, and Na_2SO_4.

It was found that the nature of the potential shift depends little on the medium. The initial potential determines the rate of potential displacement upon contact with hydrazine, which is explained by the different condition of the electrode's surface.

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The electrochemical behavior of hydrazine on platinum-group metals/107* is examined rather thoroughly in the current literature. Processes in the "double-layer region" in the absence of electrochemically active gases -- oxygen and hydrogen -- can be studied on these metals.

At the same time, the electrochemical interaction between hydra- /108 zine and oxidized surfaces possessing semiconductor properties is of some interest. From this standpoint, we chose a titanium electrode.

Hydrazine hydrate of "ch. d. a." [analytical] grade was used in our work, and the purity of the titanium electrode was 99.985; all solutions were prepared from twice-distilled products.

Since the purpose of this work was to investigate the interaction of an electrode-hydrazine system relative to the thickness of the oxide film, it proved necessary to choose a method of electrode preparation so that at the initial moment the surface was as close as possible to a metal surface free of oxide film.

The electrodes were subjected to mechanical trimming and chemical treatment in hot solutions of $1N$ sodium hydroxide (10 min) and $2N$ sulfuric acid (2 min) [1]. Then the electrode was smoothed off with powdered glass, transfered to a cell, and subjected to electrochemical treatment in $0.1N$ sodium hydroxide by a 20 mA cathode current with simultaneous passage of argon.

The study was conducted using the familiar method, described in [2].

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*Numbers in the margin indicate pagination in the foreign text.

To study the processes taking place with anode and cathode polarization, charging curves of a titanium electrode in 0.1N solutions of sodium hydroxide, sulfuric acid, and sodium sulfate were plotted (Fig. 1). These electrolytes have a very small dissolving power relative to titanium [3].
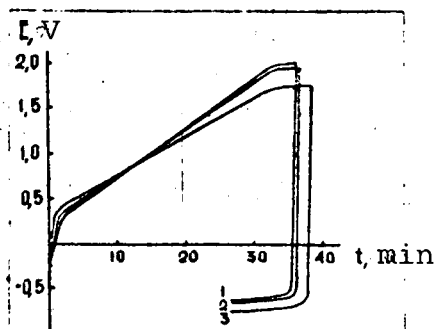

Fig. 1. Charging curves of titanium electrode in various media:

1 -- Na$_2$SO$_4$; 2 -- H$_2$SO$_4$; 3 -- NaOH.

The initial anode branch of the charging curve is characterized by a rapid shift of potential in time. This is evidence that in this section there is only surface charge transfer. A slow change in potential is characteristic of the next section. This change of potential can be explained by the fact that processes of both oxide-film growth and formation of oxides of different compositions are taking place.

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The authors of [4, 5] suggest that in this interval of potentials there is formation of Ti$_2$O$_3$ oxide and its further oxidation, according to reaction:

$$Ti_2O_3 + H_2O \longrightarrow TiO_2 + 2H^+ + 2\overline{e}.$$
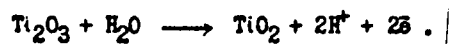
A "plateau" appears at a potential of 2 V, i.e., the potential no longer depends on the amount of electricity passed through, but no release of molecular oxygen was observed. This delay is explained by the process of anodization -- accumulation of an oxide film.

An abrupt potential change is initially observed when the cathode charging curve is plotted. In this potential region the oxide film is reduced at higher cathode potentials.

As Fig. 1 shows, the charging curves of the titanium electrode in different media are not substantially different. This allows the suggestion that the medium's pH has no significant effect on the process of oxide layer formation with anode polarization.

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The value of the initial electrode potential at which hydrazine   /110
was put on the electrode to study electron-adsorption interaction was
chosen through 200 mV on the charging curve. By changing the initial
potential by 200 mV we changed the strength of the oxide film on the
electrode and the surface charge.

When hydrazine was introduced on the titanium electrode in an
acid medium, we observed a sharp displacement of potential toward
the cathode side. As shown by oscillographic study, the rate of poten-
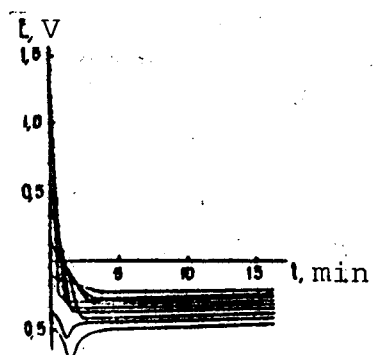tial displacement is not a constant value and depends on the initial
potential (Fig. 2).

Fig. 2. Effect of E_O on the kinetics of potential displacement upon contact between hydrazine and titanium electrode in $0.1N$ H_2SO_4.

As Fig. 2 shows, upon contact with
hydrazine the electrode potential shifts
fairly abruptly toward the cathode side, and
in 2-3 min an oxidation-reduction potential
is established. The final value of the poten-
tial of the titanium electrode in hydrazine
solutions is approximately the same in
different solutions, -0.21 - 0.24 V, and does
not depend on the initial electrode potential.

When studying the kinetics of oxidation-   /111
reduction potential establishment on a titanium
electrode in hydrazine solutions, we have to
note a fairly good convergence of the adsorp-
tion parts of the potential displacement curves when the substance
comes in contact with the electrode. This phenomenon is not observed
with potential displacement produced by electrochemical interaction
between alcohols and a platinum electrode.

It seemed interesting to study the behavior of hydrazine at initial
potentials whose values were more cathodal than the establishing poten-
tial. When the potential displacement was found using a potentiometer,
the potential was found to shift toward the anode side. But use of
the oscillographic method revealed that the potential shifts toward

the cathode side, with oscillographic return to the anode region.

Thus, at any initial potential values, there is hydrazine oxidation, the electrode potential shifts to the cathode side, and the final potential is determined by the relationship of the oxidized to the reduced form of hydrazine. Experiments performed in decinormal solutions of sodium sulfate and sodium hydroxide produced similar results.

Oscillographic study of the kinetics of potential shift revealed that when the initial electrode potential shifts toward the anode side we observe an increase in the rate of electrochemical interaction (Fig. 3).
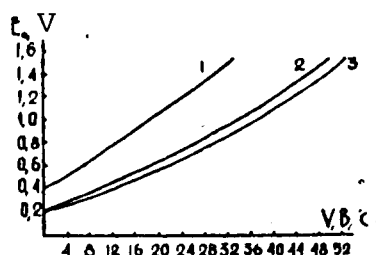

Fig. 3. Effect of E_O on rate of potential shift upon contact of hydrazine with titanium electrode in different media:

1 -- NaOH; 2 -- Na_2SO_4; 3 -- H_2SO_4.

When the initial potential is increased, an oxide film of variable composition accumulates on the electrode. Furthermore, there is adsorbed oxygen on the metal's surface. Potential displacement toward the cathode side may be explained by electrochemical removal of oxygen from the electrode's surface [6] and chemical interaction between hydrazine and surface oxygen compounds, since hydrazine solutions have reducing properties [7].

The presence on the surface of the elec-/112 trode of non-stoichiometric oxides that are n-type semiconductors [8], which do not block the surface of the electrode, may lead to electron exchange between the molecules of hydrazine and the electrode. The increase in the potential displacement rate is explained by different energy-level differentials in the molecule and in the metal.

In this case a phenomenon occurs where the increase in the rate of electrochemical interaction is determined by the accumulation of film on the electrode's surface. But in this case it is impossible

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to decide the question in favor of merely electrochemical interaction.

As mentioned above, the nature of the titanium electrode's potential shift upon contact with hydrazine depends very little on the medium. The increase in the rate of potential fall-off with shift in the initial potential to the anode region is similar in acid and neutral media (Fig. 3). The slope of the curve for an alkaline medium is more abrupt. The obtained data confirm the stated hypothesis of the formed oxide film's lack of dependence on medium pH. The rate increase upon /113 transition to an alkaline medium can be explained by a parallel reaction -- oxidation by OH^- radicals.

Conclusions

The kinetics of the establishment of the oxidation-reduction potential of a titanium electrode upon contact with hydrazine was studied in different media.

It was revealed that the nature of the potential displacement depends little on the medium. The initial potential determines the rate of potential displacement upon contact with hydrazine, which is explained by the different condition of the electrode's surface.

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